

APPENDIX H

PATENT
TH0681 04 (US)
DFH:EM

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of)
DAVID M. SINGLETON, LOUIS KRAVETZ,)
BRENDAN D. MURRAY)
Serial No. 11/748,976) Group Art Unit: 1796
Filed May 15, 2007) Examiner: Necholus Ogden Jr.
HIGHLY BRANCHED PRIMARY ALCOHOL) November 5, 2008
COMPOSITIONS, AND BIODEGRADABLE)
DETERGENTS MADE THEREFROM)

COMMISSIONER FOR PATENTS
P. O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION UNDER RULE 132

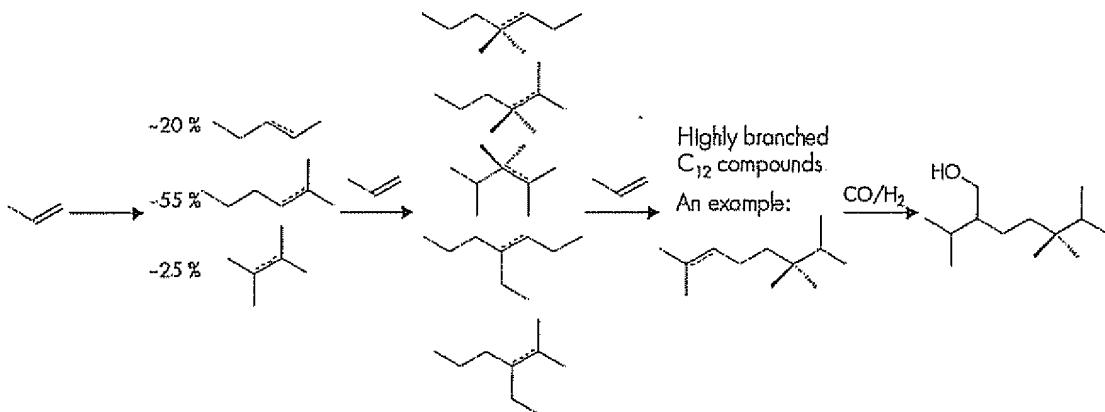
William Warren Schmidt hereby declares:

THAT he received an A.B. in Chemistry from the University of Tennessee at Chattanooga, Magna Cum Laude, in 1967; and that he received his M.S. Degree in Chemistry in 1969 from the University of Tennessee; and he received his PhD in Organic Chemistry from the University of Tennessee at Knoxville in 1975; and

THAT he has been employed by Shell Oil Company or one of its related companies since 1987 and has worked in the areas of the structure/property relationships of surfactants, the utility of alcohol-based surfactants, especially as detergent structures changed, the formulation of liquid detergents, the investigation of the detergency of alcohol ethoxylates, and the utility of alternate hydrophiles for surfactants; and

THAT, as described by Grifo, U.S. Patent No. 2,766,212, column 2, lines 9-13, the alcohols were prepared using the "oxo process" starting with olefins such as the "tetrapropylene" that was used to prepare the oxo tridecyl alcohol used in the examples; and

THAT the reaction sequence below depicts how such olefins, specifically tetrapropylene, were prepared in 1956 and displays representative structures; and that in the absence of comment or teaching, the catalyst for the olefin production is presumed to be an acid as described in Chemistry of Organic Compounds, 3rd Edition, by Noller, 1965, pp. 102-103 which describes olefin self-addition (see the bottom of p. 102 for mention of propylene tetramer); and



propene (I) \rightarrow dimers (II) \rightarrow trimers (III) \rightarrow tetramers (IV) \rightarrow isotridecanols (V)

THAT the dimers (II) will be approximately 80% branched and 20% linear and when the next propene is added, a very complex mixture (III), with little, if any, residual linear olefin is formed (five of the many possible structures are shown and three of the five structures have a quaternary carbon); and with the addition of the fourth propene, a complex mixture of greater than twenty olefins (IV), many of which have a quaternary carbon, is formed (only one of these has been drawn, a tri-methyloctene with a quaternary carbon); and that the use of an acidic catalyst facilitates alkyl group migration, thus increasing the number of isomers and the complexity of the structures; and

THAT the oxo reaction (V) with carbon monoxide and hydrogen yields a similarly complex mixture of alcohols which will also contain quaternary carbons (again only one of many possible isomers has been depicted); and

THAT the oxo tridecyl alcohols made by Grifo would have been comprised of many isomeric structures, a substantial number of which would have had quaternary carbon atoms and that the mixture would have had much more than 0.5 atom percent of quaternary carbon atoms; and that the oxo tridecyl alcohols would have exhibited poor biodegradability.

William Warren Schmidt further declares that all statements herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date November 5, 2008

William Warren Schmidt
William Warren Schmidt

3rd Edition

CHEMISTRY
of
ORGANIC
COMPOUNDS

CARL R. NOLLER
Professor of Chemistry, Stanford University

W. B. SAUNDERS COMPANY
Philadelphia and London

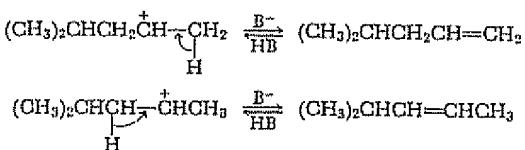
1965

Self Addition (Polymerization). An alkene molecule in the presence of an acid catalyst can add another molecule to give a new alkene. The product has twice the molecular weight of the original alkene and is called a *dimer* (Gr. *meros* part, hence *two parts*). The original alkene is called a *monomer*.

The initial step is the same as that for the addition of an acid or of water to the double bond. The catalyst adds a proton to the monomer according to the Markovnikov rule to yield a carbonium ion. This intermediate carbonium ion is a Lewis acid and adds to the second molecule to give a new carbonium ion.

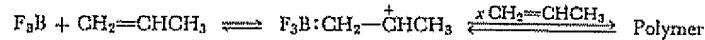


The second carbonium ion can be stabilized by loss of a proton to a base with the formation of a double bond, but since the proton can be lost from either carbon adjacent to the carbonium carbon, a mixture of two olefins results.



In this representation of steps and in subsequent equilibrium reactions illustrating stepwise mechanisms, a convention is adopted that eliminates the necessity of rewriting formulas. The catalyst or reagent is placed above the double arrow and the minor product that is eliminated is placed below the double arrow. The interpretation of the first reaction is that the acid HB transfers a proton to the methylene (CH_2) group of 1-butene with loss of the base B^- to give the intermediate carbonium ion. In the second and third equations, a base B^- removes a proton from a carbon atom adjacent to the carbonium carbon with regeneration of the acid HB and the formation of the hexenes. In the reverse reactions, the reagent is below the arrow and the minor product is above the arrow. It will be observed that reactants that appear above and below the arrows cancel each other and do not appear in the final products.

Reaction of the dimeric carbonium ion with a third molecule of alkene gives a trimeric carbonium ion, which can give a mixture of *trimers*. It can react also with a fourth molecule of alkene to give a mixture of *tetramers*. It should be noted that the product always contains one double bond and that all of the steps are reversible. This process can repeat itself until products of high molecular weight are obtained. The reaction is strongly exothermic because at each step a π bond is replaced by a carbon-carbon bond with the liberation of about 20 kcal. of energy. The products may be considered to be made up of many small parts and are called *polymers* (Gr. *polys* many, *meros* part). The process by which they are formed is called *polymerization*. If, as with the alkenes, polymerization takes place by addition, it is known as *addition polymerization*, and the product is an *addition polymer*. Although the acid catalyst was symbolized by the general formula HB, and although phosphoric or sulfuric acid is the usual catalyst, Lewis acids such as boron fluoride or aluminum chloride also initiate polymerization.



The acid-catalyzed polymerization of alkenes is important commercially for the production of alkenes of medium molecular weight and of polymers of high molecular weight. Propylene trimer and propylene tetramer have been the chief intermediates in the manufacture of synthetic detergents (pp. 819, 507). They are made by passing propylene over a catalyst consisting of a film of

ence of an acid catalyst twice the molecular weight (two parts). The

water to the double Markovnikov rule to acid and adds to the



base with the formic acid adjacent to the

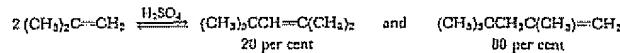
reactions illustrating the minor product of the first reaction of 1-butene with loss and third equations, cationium carbon with reverse reactions, the. It will be observed and do not appear

ene gives a trimeric in a fourth molecule but always contains in repeat itself until exothermic because iteration of about 20 in small parts and they are formed is ace by addition, it. Although the acid phosphoric or sulfuric m chloride also ini-

polymer

be production of propylene trimer synthetic deter-
ting of a film of

phosphoric acid on quartz granules. If isobutylene is passed into cold 60 per cent sulfuric acid and the solution is heated to 100°, a mixture of dimers and trimers (about 4:1), together with smaller amounts of higher polymers, is formed. The mixture of dimers is known as diisobutylene and consists of four parts of 2,4,4-trimethyl-1-pentene and one part of 2,4,4-trimethyl-2-pentene (cf. p. 96).



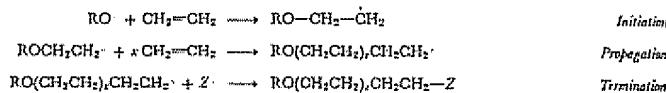
Catalytic hydrogenation of the mixed diisobutylene yields 2,2,4-trimethylpentane, the standard 100-octane motor fuel (p. 110).

The trimers and higher polymers are formed by reaction of the dimers with more isobutylene. If boron fluoride or anhydrous aluminum chloride is used as a catalyst at -100°, polyisobutylenes having from 400 to 8000 C₄H₈ units and varying from sticky viscous resins to elastic rubber-like solids are obtained.

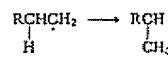


The acid-catalyzed polymerization of olefins gives as products only viscous semisolids of high molecular weight. In 1938 a patent was issued in Great Britain for the production of a solid polymer of ethylene. The polymerization is carried out above 100° and at pressures above 15,000 p.s.i. in the presence of 0.01 per cent of oxygen. The molecular oxygen, with its two unpaired electrons of like spin (p. 14), acts as a free radical initiator. Free radicals generated by the thermal decomposition of organic peroxides (p. 101) also may be used.

The free radical, RO[·], starts a chain reaction (p. 47), which is terminated by the union with any other free radical, Z[·], with which the growing chain may collide in the proper way. Usually Z[·] is another growing chain.



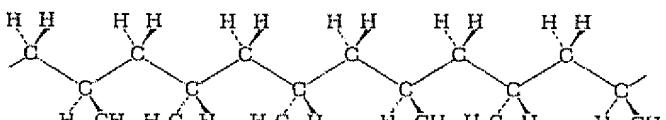
The product, called polyethylene, is a linear polymer but contains about one methyl branch for every 8 to 10 methylene (CH₂) groups. The branching results from the occasional shift of a hydrogen atom during the polymerization.



Various catalysts, such as the so-called Ziegler catalysts, for example titanium tetrachloride and an alkylaluminum (p. 130), have been developed that not only permit polymerization to take place at essentially atmospheric pressure but also reduce the amount of branching and yield a denser and more rigid polymer called *high density polyethylene*.

The polyethylenes are *thermoplastic*; that is, they soften and flow on heating because the molecules can slip past each other. In this condition they can be extruded into sheets and various shapes, which solidify on cooling. Because polyethylenes are saturated hydrocarbons, they are very inert, and their high molecular weight makes them insoluble in most solvents. During 1963, United States production reached 2.3 billion pounds.

In the polymerization of substituted olefins such as propylene, the usual catalysts give a random spatial arrangement of the polymeric units as in (a) with the result that the attractive forces between the chains are not strong, and the products are oils and sticky semisolids. The catalysts that produce high density polyethylene (p. 103), however, give an ordered arrangement of the polymeric units as in (b) with the result that a useful product is obtained. Polymers with a random arrangement of units are said to be *atactic* (Gr. *an* not,



(a) Section of atactic polypropylene chain.